BAP IMPACT ASSESMENT USING A MODIFIED VERSION OF CMAQ MODEL OVER ZARAGOZA (SPAIN)

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Abstract: Benzo(a)pyrene (BaP) is polycyclic aromatic hydrocarbon whose adverse effects on human health have been demonstrated. Directive 2004/107/CE of the European Union establishes a target value of 1 ng/m3 of BaP in the atmosphere. In this contribution we have used the third generation of air quality modelling systems to evaluate the impact of BaP emissions in Zaragoza area (Spain) with 1 km spatial resolution. We have developed the inclusion of the transport, scavenging and deposition processes for the BaP. BaP degradation and adsorption mechanism have also been integrated into the chemical-transport model CMAQ (Community Multiscale Air Quality Modelling System). BaP is injected into the atmosphere as particle.The aerosol-gas partitioning phenomenon in the atmosphere is modelled taking into a count that the concentrations in the gas and the aerosol phases are in equilibrium. The WRF (Weather Research & Forecasting Model)) is also used to provide the meteorological information as input for CMAQ modelling system. A validation process of the BaP and other pollutant results have been conducted in the urban area of Zaragoza (Spain) during 12 weeks since February, 2010 to January, 2011. The agreement is generally satisfactory.

Key words: *Health, air pollution, MM5, CMAQ, relative risk, epidemiological studies, C-R functions*

INTRODUCTION

Directive 2004/10/CE of the European Union, establishes a target value of 1 ng/m^3 to the air pollutant Benzo(a)pyrene (BaP). Besides the target value the European Union also defined an upper and a lower assessment threshold of 0.6 and 0.4 ng/m^3 per annum. If BaP concentrations exceed an assessment threshold, national authorities are obliged to monitor the atmospheric concentration of BaP. For areas with BaP concentrations between the assessment thresholds, the directive allows to determine the atmospheric burden with the help of modes instead of observations. BaP is one of the most important polycyclic aromatic hydrocarbons (PAHs) with adverse effects on human health because of their carcinogenicity (Pedersen et al., 2005). BaP is often used as an indicator for the total burden of carcinogenic PAHs.

BaP is semivolatile compound that can be transported in the atmosphere over large distances either as gaseous species or while bound to fine particles and can be easily inhaled into the residents (Jathar et al., 2012). BaP obviously undergo long-range atmospheric transport such that remote areas far from the emission are exposed. Its lifetime in the atmosphere depends on its vapor pressure, affinity to water and organic solvents, and its resistance to photolyc and photochemical degradation (Scheringer et al., 2001).

Although BaP in ambient air has been studied in some European cities, few studies had been conducted in Spain. Modeling can help to assess the spatial and temporal distribution of BaP concentrations across domains and to also assess the impact of different emission reduction scenarios. It was necessary to simulate the atmospheric transport of the BaP considering dynamic atmospherics processes in addition to pollutant properties. To simulate adequately the processes that determine the transport, degradation and deposition of BaP and other PAHs, it is essential to have a chemical transport model that represents the state of the art in atmospheric modeling as well as in aerosol chemistry and dynamics. BaP is bound to aerosol particles. In the atmosphere gas and particulate phases are differently affected by degradation and deposition processes. Accurate calculation of gas/particle partitioning on a regional/local scale requires information about the spatially and temporally resolved physical characteristics and chemical compositions of atmospheric aerosols.

METHODS

The Community Multiscale Air Quality (CMAQ) model of the USE EPA, 4.7.1 version (June 2010) is used. This Eulerian modelling system can be used to model the atmospheric distribution of air pollutants and aerosols including aqueous chemistry, from regional to local scales. The CMAQ already includes a detailed representation of atmospheric aerosols and it can be expanded to other substances. In this experiment CBO5 chemical mechanism (Yarwood et al. 20015) is used with the Euler Backward (EBI) solver. CMAQ can be conveniently linked to the mesoscale meteorological model Weather & Research Forecasting system (WRF) developed by NCAR and others, which is used here to calculate the meteorological input fields so CMAQ model is driven by WRF meteorological model with 1 hour temporal resolution. WRF model can be directly linked to CMAQ via a Meteorological Chemistry Interface Preprocessors (MCIP). The 3.3.1 version (September 2011) is setup with the following physics options: PBL scheme and diffusion, Yonsei University (YSU) PBL (Hong, S.-Y. and Dudhia, J. (2003)); Explicit moisture scheme, Lin microphysics; Radiation schemes, Rapid radiative transfer model (RRTM) longwave radiation and Simple cloud-interactive shortwave radiation scheme Dudhia radiation.

In this contribution, the extension to CMAQ (CMAQ-BaP) is summarized. A new extended version of CMAQ (CMAQ-BaP) has been developed to investigate BaP spatial and temporal distribution over Zaragoza area. The basic version of CMAQ is modified to read the emissions and to simulate the transport, scavenging, and deposition of BaP. CMAQ wet deposition includes rainout and washout from convective precipitation and scavenging. Two new BaP species have been added, aerosol (BAP) and gas (SV_BAP). BaP in gas phase is treated as inert gas because BaP in the gas-phase primarily react with OH although, the representative lifetime with respect to reaction with OH is higher than BaP in the particulate-phase [20]. BaP is emitted in particle phase, 99% accumulation mode (0.1 – 2.5 um) and 1% Aitken mode (< 0.1 um). Deposition and scavenging of the aerosol BaP is the same parameterizations as for CMAQ organic aerosols. Deposition velocity of BaP gas is the same that the semi-volatile alkanes that is calculated by CMAQ.

The gas-particle partitioning has a substantial effect on transport in case of BaP. New developments to simulate gas phase and organic carbon(OC)-bound particulate transport and chemistry have been added. The BaP extension to CMAQ calculates the partition of the compound between the gas and the particle phase according to Equation 1.

$$C_{aer} = C_{tot} - C^{*}_{sat} \frac{C_{aer}/m}{Tot_{org}} \qquad (1)$$

C_{aer} : Concentration in the particle phase
C_{tot} : Total concentration (gas + particle)
C^{*}_{sat} : Saturation concentration
m : Molecular weight
Tot_{org} : Total abosorbing organic mass

Saturation concentration (C^{*}_{sat}) is modified as a function of temperature using the Equation 2:

$$C^{*}_{sat} = C_{sat} * T_{factor} \qquad (2)$$

where C_{sat} is the effective saturation concentration with a value of $5.4e^{-3}$ (µg/m^3) and the temperature factor T_{factor} is calculated as Equation 3:

$$T_{factor} = \frac{T^0}{T} e^{\left(\frac{\Delta H_{vap}}{R}\left(\frac{1}{T^o} - \frac{1}{T}\right)\right)} \quad (3)$$

T^0 : Reference temperature (298 ºK)

T : Air temperature

ΔH_{vap} : BaP Enthalpy of vaporization (116.7e3 J/mol)

R : Gas constant (8.314 J/mol ºK)

Absorptive mechanism plays the dominant role in the air affected by urban sources, although adsorption mechanism would be important when atmospheric particulate material is comprised solely of mineral materials, urban particulate material generally contains a significant amount of amorphous organic carbon. An OC absorption model is implemented to model gas-particle partitioning of BaP bases on the absorptive partitioning model of Pankov (Pankow J.F. (1994) and Odum (Odum et al., 1996).

The reaction of ozone with particulate BaP is a non-linear process. Assuming a Langmuir-Hinshelwood type reaction, the life time of particulate BaP depends on the ability of ozone to bind to the particle substrate [23]. The reaction is mainly driven by the ozone concentration and the chemical composition of the particle BaP. It is incorporated also BaP loss due to oxidation by Ozone (O_3) with a first order reaction. Reaction with ozone can be an important degradation pathway for the particulate BaP in the atmosphere. Degradation of the aerosol BaP by the Ozone has been implemented into CMAQ based on [23] following the Equation 4. Heterogeneous reactions are considered to be more important than gas-phase reactions as an atmospheric sink

$$K = \frac{K_{\max} K_{O_3}[O_3]}{1 + K_{O_3}[O_3]} \quad (4)$$

K : Degradation rate constant

$K_{\max}$: Maximum rate coefficient (0.06 s^{-1})

K_{O_3} : Ozone gas to surface equilibrium constant (0.028 $10^{-13} cm^3$)

$[O_3]$: Ozone conentratrion

The mother modeling domain is a Lambert Conformal Conic projection centered at 41.69N, 0.89W, with 67 x 55 grid squares of 27 km resolution for Iberian Peninsula. Three nesting domains have been setup centered over Zaragoza city. First nesting level is 49 x 49 grid squares of 9 km resolution, second 31 x 37 of 3 km and finally 28 x 28 of 1 km resolution. 15 vertical terrain following levels up to 100hPa have been selected.

The accuracy of simulations depends strongly on emission data and unfortunately there are uncertainties in BaP emissions [24, 25]. The main source of BaP is incomplete combustion processes of organic material, in particular wood and coal in private households. Industrial heating and cookeries as well as road traffic are also large sources of BaP [26]. Emission of BaP are emitted as particle phase

BaP global emission coming from EMEP inventory with 0.5 degrees of spatial resolution. A projection process from source grids to lambert conformal conic domains was developed through an interpolation process with mass conservation. The BaP emissions are broken down into the SNAP 12 categories, Table 1. In case of high resolution domains (1Km, 3Km and 9 Km) a top- down process scheme has been used to going to the desired resolution. The downscaling process is based on surrogates to allocate the emission into the model grid. Different surrogates are used for different SNAP´s activities, Table 1

Table 1. Weights and surrogates for the emission snap activities

SNAP ACTIVITIES	WEIGHT	SURROGATES
Combustion in energy	15.0 %	Industrial areas
Non-industrial combustion	23.0 %	Buildings
Combustion in manufacturing	15.0 %	Industrial areas
Production processes	5.10 %	Industrial areas

Extraction of fossil fuels	8.40 %	Mineral extraction
Solvent use	0.50 %	Industrial areas
Road transport	29.7 %	Roads and streets
Other mobile sources	0.10 %	Roads
Waste treatment	3.00 %	Waste areas
Agriculture	0.20 %	Natural areas

Model runs for 12 weeks (11 weeks from 2010 and 1 from 2011) corresponding to the field campaign are used to examine the model results under very different meteorological conditions. The model run was started one day before the time period of interest began to avoid the influence of the initial conditions.

RESULTS AND CONCLUSIONS

One monitoring site providing daily BaP concentrations of BaP has been used to validate the new CMAQ-BaP model. The BaP monitoring data are coming from a PAH field campaign developed by ICB-CSIC. The "Instituto de Carboquímica (ICB)" is a public research Centre belonging to Spanish National Research Council (CSIC). Figure 1 shows the comparison of the measured mean values with the calculated values from simulations in a scatterplot. It suggests that the correlation between measured and simulated values is good, as also indicated by Pearson´s correlation coefficient r of 0.86.

The agreement is generally satisfactory, the best results are observed in winter period, which is the most important for the BaP concentrations. The model validation shows the BaP extension performance is correct over the modeled area. The BaP concentrations agree well with the observations, particularly very high B(a)P peaks are resolved by the extended model. The modeling system reproduces the degree of seasonality of the BaP, with higher concentrations in the winter months. This is particularly prevalent at urban locations, where domestic combustion is the major source. In the rest of areas, for example industrial zones, concentrations are affected by other meteorological parameters, temperature, boundary layer, wind speed and direction

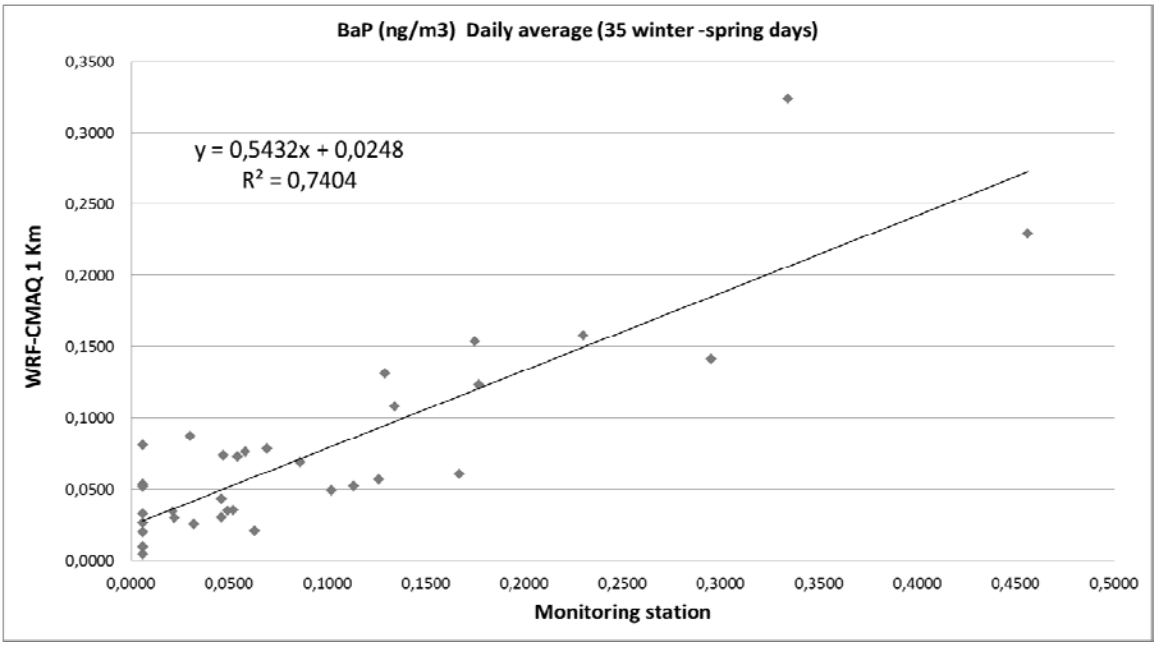

Figure 2. Linear regression of BaP model 1Km. resolution (y axes) and BaP monitoring station (x axes). Daily average during 35 winter and spring days. R=0.86.

CONCLUSIONS

WRF-CMAQ modeling system, which has been extended to simulate BaP concentrations, can be used to get the spatial and temporal distribution of BaP concentrations across large areas domain and to also assess the impact of different emissions reduction strategies. The evaluation results in this paper suggest that the new CMAQ-BaP is able to simulate fairly well the ambient air concentrations of BaP. For further verification of the model performance, long-term runs will be carried out and more measurement points will be used. The results of the new tool presented show that it can constitute an important tool to help city planners to comply with the environmental regulation. The results can be used to interpret the relative differences between ON and OFFs scenarios with corresponding error margins and quantify the impact on the area of the different emission reduction strategies. This approach allows quantifying the impact of different source types on atmospheric BaP concentrations.

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REFERENCES

Hong, S.-Y. and Dudhia, J. (2003) Testing of a new non-local boundary layer vertical diffusion scheme in numerical weather prediction applications. In: Proceedings of the 16th Conference on Numerical Weather Prediction, Seattle, WA.

Jathar, S. H., Miracolo, M. A., Presto, A. A., Nguyen, N. T., May, A. A., Adams, P. J. and Robinson, A. L. (2012) Modeling the formation and properties of secondary organic aerosol from the photo-oxidation of low volatility organics: Problem formulation and application to aircraft exhaust. Atmos. Chem. Phys. 12, 9945-9983.

Pankow J.F. (1994) An absorption model of gas-particle partitioning of organic compounds in the atmosphere. Atmospheric Environment 28, 185-188.

Pedersen, D. U., Durant, J. L., Taghizadeh, K., Hemond, H. F.,Lafleur, A. L. and Cass, G. R. (2005). Human cell mutagens in respirable airborn particles from the northeastern United States. Quantification of mutagens and other organic compounds. Environmental Science & Technology 39, 9547–9560.

Scheringer, W., Hungerbuhler, K. and Matthies, M. (2001) The spatial scale of organic chemicals in multimedia fate modelling. Recent developments and significance for chemical assessment. Environmental Science Pollution Research 8, 150-155.

Yarwood, G., Rao, S., Yocke, M. and Whitten, G. (2005) Updates to the Carbon Bond Chemical Mechanism: CB05. Final report to the US EPA, RT-0400675.